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POLAROGRAPHIC DETERMINATION OF NTA

Thomas B. Hoover

Environmental Protection Agency
Athens, Georgia

June 1973

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Polarographic Determination of NTA

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POLAROGRAPHIC DETERMINATION OF NTA

by

Thomas B. Hoover
Southeast Environmental Research Laboratory
College Station Road
Athens, Georgia 30601

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ABSTRACT

Pulse differential polarography was found to be a more sensitive and precise method than linear sweep voltammetry for the determination of NTA as the bismuth complex in natural and waste waters. Indium was a less satisfactory complexant. Relative standard deviations of less than 5% were obtained by the dual cell pulse differential technique at 1 ppm NTA and calibrations were linear from 0.01 to 4 ppm. Copper, added at concentrations greater than 10^{-5} *M*, caused low analytical results for NTA. No other significant interference by metals or complexants was found. An acetate electrolyte was much better than chloride for the determination of bismuth-NTA complex in sewage-type samples. Recommended procedures are given in the Appendix.

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Sydney H. Young assisted with the studies on indium.

SECTION I

CONCLUSIONS and RECOMMENDATIONS

Nitrilotriacetic acid (NTA) was determined with a standard deviation of 3 µg/ℓ in natural and waste waters as the bismuth complex using dual-cell pulse differential polarography.

Indium was a less satisfactory complexant than bismuth for the determination of NTA.

An acetate electrolyte gave better results in sewage type samples than a chloride electrolyte. The acetate electrolyte is therefore recommended for the polarographic determination of NTA in natural waters and waste waters containing less than 0.1 percent chloride. A chloride electrolyte is recommended for saline samples. Analytical procedures for both are given in the Appendix.

Linear sweep (LS) voltammetry was a more rapid analytical technique than pulse differential (PD) polarography, but was less sensitive. Dual cell PD is therefore recommended for analyses in which the greatest sensitivity and precision are required. Dual cell LS is recommended for routine and repetitive analyses when the highest precision is not needed.

The effects of possible interference by metal ions and complexants were evaluated. Copper at concentrations greater than about 1 mg/ℓ may lead to low results for NTA.

Linear calibration curves for the determination of NTA were obtained for the concentration range of 0.01 to 4.0 mg NTA/ℓ, according to the recommended procedures in the Appendix.

SECTION II

INTRODUCTION

Nitrilotriacetic acid (NTA) was used briefly as a builder in laundry detergents, partially replacing polyphosphate. The high degree of biodegradability of NTA makes its use attractive, especially in regions where detergent phosphates contribute materially to eutrophication. On the other hand, the potential health hazards of NTA in the environment that have led to a moratorium on its use (1) dictate that reliable analytical methods should be available for monitoring the build-up of NTA in the environment should commercial use be resumed.

Many analytical methods for NTA have been developed, most of which utilize complexation with metals for the separation or determination. Colorimetric methods have been based on the measurement of Fe(III) (2), Cu(II) (3), or Zn(II) (4,5) with appropriate color reagents. Swisher (2) separated NTA as the Fe complex, together with any other soluble Fe complexes, decomposed the complexes, and determined the resulting Fe. The other authors above measured the excess metal ion after reaction with complexants in the sample. Consequently, these methods are not specific for NTA unless elaborate separation procedures are used. The zinc-zincon colorimetric procedure (5) has been automated to provide rapid analyses with relative standard deviations of 2-10% in the concentration range 0.1 to 10 mg NTA/ℓ. However, several metal ions cause negative interference, sewage-type samples give high results, and the method is not applicable to saline waters.

The Cu-NTA complex has been employed analytically, with a copper-ion selective electrode as the detector (6,7). Like the colorimetric procedures, this technique lacks specificity but it is especially suitable for continuous monitoring (6) or for complexometric titrations (7).

Methods employing gas chromatography (gc) (6,8,9,10) determine NTA directly as a suitably volatile ester, and thus have an important advantage of specificity. On the other hand, the determination of total NTA requires its separation from complexing metals, generally by ion-exchange pretreatment, with the possible loss of NTA

(11). Furthermore, to esterify the NTA, substantially all the water must be removed by evaporation. This step is lengthy and may lead to losses (6). The better of the gc methods require injections of at least 0.2 µg as NTA and give relative standard deviations of 7 to 13% (9,10).

Polarographic methods are based on the reduction of a suitable metal ion complexed with NTA. Since the half-wave potentials for the reduction of several complexes of the same ion usually vary appreciably according to the ligand, this procedure is nearly as specific for NTA as are the gc methods. In fact,some of the earliest polarographic studies were made for the purpose of resolving a series of similar chelating agents (12) or for determining NTA as an impurity in EDTA (13,14).

The objectives of this project were

- to develop and evaluate an analytical method for NTA that would determine 10 µg/ℓ or more with 15% accuracy in seawater and in waste water, and

- to evaluate and compare some of the newer polarographic techniques of high analytical precision, specifically, pulse differential polarography (PD) and linear sweep voltammetry (LS).

SECTION III

EXPERIMENTAL

INSTRUMENTATION

The experimental plan was significantly influenced by the type of instrumentation that could be obtained and by the equipment purchase schedule. The first analytical instrument obtained, and work horse for the entire project, was a Princeton Applied Research (P.A.R.) Model 170 Electrochemistry System. It is one of a few general-purpose electroanalytical instruments (15) that offer great versatility in types of experiments that can be conducted and range of parameters that can be controlled. It was selected primarily for its pulse polarography capability, a relatively new technique having great sensitivity.

In the pulse differential (PD) mode, the current is sampled and its value stored twice during the life of each drop from the mercury electrode. These measurements are taken before and after a square potential pulse of 50 mV is applied to the electrode on top of a continuous ramp potential that may be increasing a few mV during the life of the drop. The pulse excitation wave form is shown schematically in Figure 1. The second current measurement is taken after sufficient time has passed (about 40 msec) to allow the charging current associated with the pulse to decay to an insignificant level. The difference between two current measurements on the same drop gives a derivative-type of polarogram (Figure 2) that is nearly independent of random fluctuations in drop size. The 48 msec measurement cycle is completed near the end of the drop life, when the drop size is changing slowly. The technique is especially useful for trace determinations because the effect of the residual current is removed automatically in the subtraction step.

The P.A.R. Model 172 Mercury Drop Timer is an essential component of the PD system because it provides accurate drop times of 0.5, 1, 2, or 5 seconds precisely synchronized with the current measurement. The timer dislodges the mercury drop from the capillary using opposing solenoids that give a nearly vibrationless acceleration to the capillary.

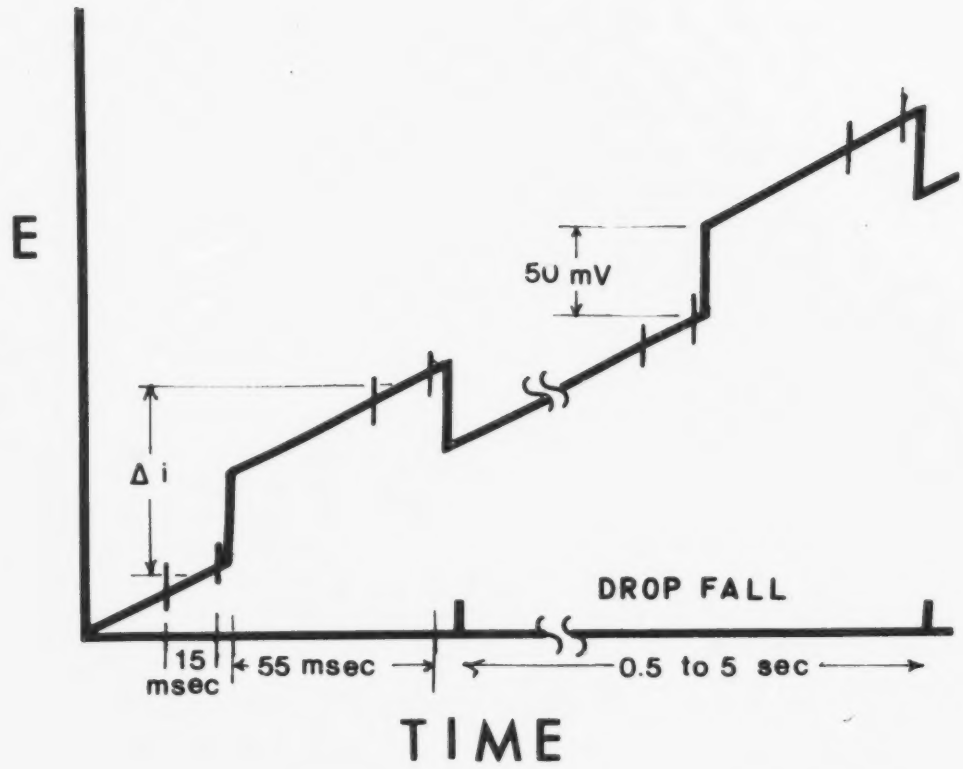

Figure 1. Excitation waveform for pulse differential technique

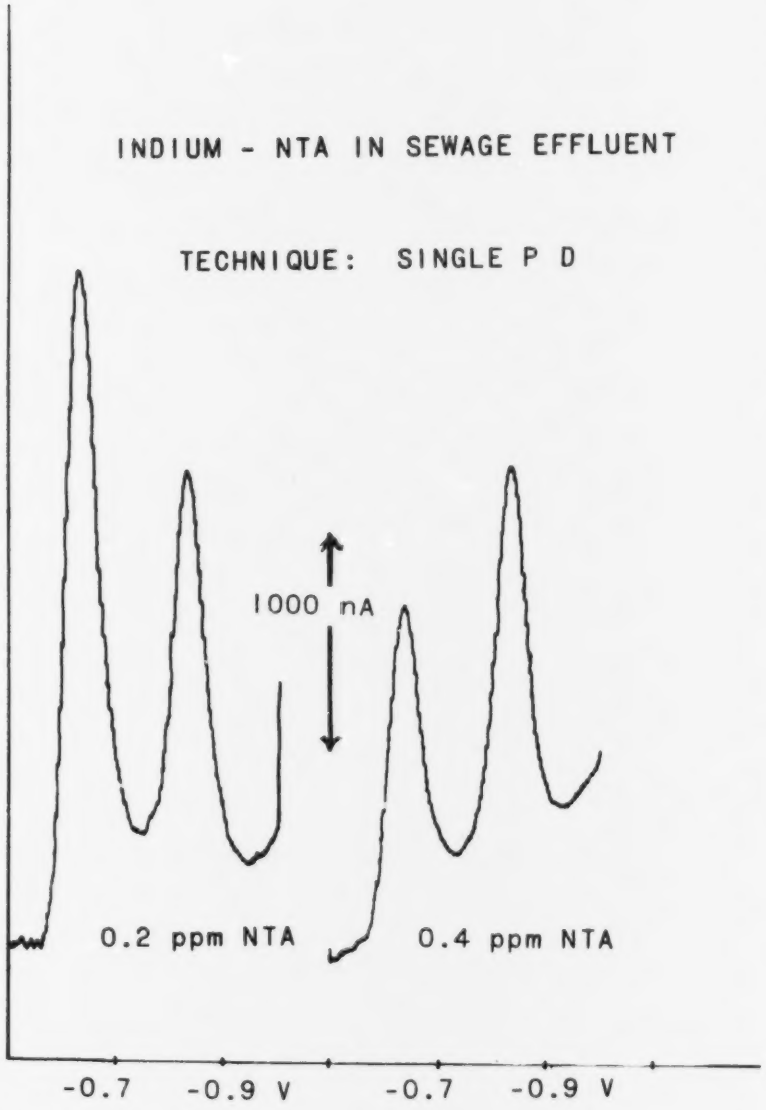

Figure 2. Determination of the indium-NTA complex in sewage effluent by pulse differential polarography

A Chemtrix Model SSP-5A Polarographic System was obtained to provide a more direct comparison with the dual-cell linear-sweep (LS) voltammetric technique used by Afghan and Goulden (16,17). Although the Model 170 provided LS programming, it was not designed for dual cell work, the voltage sweep was not synchronized with the DME, and sweep rates were limited to less than 0.5 V/sec by the X-Y recorder.

On the other hand, the Model SSP-5A was designed for dual dropping mercury electrodes and provided sweep rates from 0.05 to 20 V/sec. The current-potential response of the cell was displayed on a Tektronix Type 564B storage oscilloscope and a Tektronix camera system provided a permanent record of the traces (Figure 4). The polarographic programming and amplification circuitry were supplied as two special plug-in modules for the oscilloscope and drop timing was controlled by a solenoid on the electrode stand. Drop times were continuously variable from about 0.5 to 10 sec by an R-C timing circuit. When the solenoid closed it tapped the capillaries to dislodge a drop from each and simultaneously sent a pulse to the programming module to initiate the polarographic sequence.

Near the end of the project the P.A.R. Model 174/51 Linear Sweep Module Accessory became available, together with an adapter kit to allow its use with the Model 170. This modification made possible dual cell operation in either PD or LS modes. The output of the LS mode was displayed on the Tektronix oscilloscope, using general-purpose plug-in modules 3A75 and 3B3 Time Base.

After some experimentation the cells for use with either instrument were made from 18 x 75 mm test tubes of borosilicate glass or polycarbonate. Platinum leads were sealed in the bottoms to make contact with the mercury anode and plastic caps were made with holes for the capillary, for the nitrogen inlet (2-mm polyethylene tubing), and for the sample introduction. In most experiments the cathode potential was controlled with respect to the mercury pool. When reference electrodes were used they were made of silver wire anodized in a chloride solution. The salt bridge consisted of a 3-mm glass tube, drawn to a tip, plugged with filter paper, and filled with saturated KCl. The reference electrodes were periodically compared with a Beckman SCE or with the reference electrode of a combination glass pH electrode.

INDICATOR CHOICE

The choice of metal ion to be used as a polarographic indicator for NTA depends somewhat on the objective of the analysis. To determine total NTA in natural or waste waters one should use an ion that forms a sufficiently strong complex to displace all other ions that are likely to be present in significant concentrations. On the other hand, to determine free NTA in the presence of natural complexes one should select an indicator ion that does not appreciably displace the equilibria among ions naturally present in the sample but forms a sufficiently strong complex with NTA to give an identifiable polarographic wave. The stability constants of complexes of NTA with many metals have been determined in fundamental studies of chelation (14,18,19).

A second consideration in the choice of an indicator ion is the resolution that can be obtained in a complex mixture. Since the width of a polarographic wave is inversely proportional to the number of electrons involved in the electrode reaction, a three-electron reduction will give a sharper, more easily identified wave than two-or one-electron reductions. Bi(III) (6,17) and In(III) (20) have been preferred for the determination of total NTA, although methods have also been based on Cd(II) (21,22,23), and Pb(II) (17).

INDIUM COMPLEXATION

Studies of the indium-NTA complex were made to determine whether NTA could be measured reliably in the presence of a considerable excess of indium. Afghan (24) and Taylor (6) raised an objection to the use of indium because the In-NTA complex has a half-wave potential within 200 mV of that for free indium. A large excess of the reagent therefore tends to obscure the In-NTA wave. Haberman (20) solved this problem by titrating the sample with indium reagent until a free In(III) wave just appeared. He then used this wave as a baseline for the following In-NTA reduction. He showed, however, that up to 2-fold excess In did not change the indicated concentration of the NTA more than 10%.

A second problem with excess indium arises from the recognized tendency of indium in many media to show dc polarographic minima (25,26,27) rather than a

constant diffusion current. This behavior would cause a downward-sloping baseline for the In-NTA peak in the PD mode of measurement.

A stock solution of indium (1×10^{-3} *M*) was made from $In(NO_3)_3$ (Alfa inorganics) in 0.5 *M* NaCl buffered to pH 4.7 with 0.1 *M* acetate (20). Preliminary trials indicated that flatter baselines for the In-NTA peak were obtained if additional acetate (or tris(hydroxymethyl)aminomethane) buffer was not added to the sample solutions. Consequently, calibration curves were run in 0.2 *M* NaCl supporting electrolyte, or in 60% seawater, with indium stock solution added to give the desired total In concentration (usually about 1×10^{-5} *M*).

The effect of pH was studied in a series of solutions containing 1 ppm NTA (as the acid form, $C_6H_9O_6N$) and 100% excess In in 0.2 *M* NaCl. The pH was adjusted with dilute HCl in 0.5-unit steps from pH 2.5 to pH 4.5. The results, summarized in Table 1, indicate that the widest peak separation and greatest response to In-NTA were obtained at pH 4.0-4.5, where the flattest baselines were also observed. In another, more limited trial, however, better baselines were found at pH 3.0. In subsequent work, 0.2 *M* NaCl adjusted to pH 4.0 was adopted as the standard supporting electrolyte.

Since the literature contains no data on the polarographic parameters for the reduction of the In-NTA complex, solutions containing 100% excess indium were studied by dc polarography, LS voltammetry, and chronoamperometry. It was assumed, without independent verification, that a 1:1 complex was formed (28). Under the above conditions, approximately equal limiting currents were observed for the free In and for the complex. These studies confirmed that the indium wave in a chloride medium is reversible and diffusion-limited, and involves a 3-electron transfer.

The diffusion current constant, *I*, in the usual units of mA-ℓ $sec^{1/2}$ $mole^{-1}mg^{-2/3}$, was 5.9 ± 0.5 for artificial drop times of 0.5 to 2 sec and 5.5 ± 0.5 for natural drop times of 3-8 sec; *m* values were in the range 0.7-2.3 mg/sec. DeSesa et al. (29) found a diffusion current constant of 3.7 in an acetate medium.

Table 1

Effect of pH on the Polarography of In-NTA in 0.2 *M* NaCl

pH	$E_{1/2}$(vs Ag,AgCl)	$\Delta E(In^{3+}$-In-NTA)	In-NTA,i_p
2.5	-0.72 V	90 mV	0.158 μA
3.0	- .75	120	.254
3.5	- .76	130	.294
4.0	- .79	160	.335
4.5	- .82	190	.312

$E_{1/2}(In^{3+})$ = -0.63 V (Ag,AgCl)

The In-NTA wave was also diffusion limited and showed a polarographic minimum, as reported by Haberman (20). The reduction apparently was pseudo-reversible, as reported by Staroscik (28) for an acetate electrolyte, since the combination of LS and chronoamperometric data (30) led to anomalously low values for n (less than 0.5 electron). I was markedly dependent on drop time, with values of 3.1 $\pm$ 0.4 for artificial times of 0.5 to 2 sec and 9.8 $\pm$ 0.8 for natural times of 2-8 sec.

BISMUTH COMPLEXATION

The Bi-NTA complex is the basis for an automated analytical method for NTA, using LS (16) and was proven applicable to seawater samples (31). The present work was undertaken primarily to evaluate the PD technique as a means of increasing analytical sensitivity. The Chemtrix instrument was obtained to provide a nearly direct comparison with the Afghan (17) procedure. In the course of the investigation considerable interference was encountered in sewage-type samples and an acetate electrolyte was developed to overcome these problems.

The chloride media were based on those used by Afghan (16). The final analysis solution was about 0.1 *M* in total chloride (from NaCl or HCl), and contained bismuth, diluted in the sample to give 100% excess (using bismuth stock solution — 1 x 10^{-3} *M* $BiCl_3$ in 1 *M* HCl). The final pH was adjusted to about pH2. When interference from iron was suspected 0.02%, $NH_2OH \cdot HCl$ was added. In seawater the added chloride was omitted and the sample was diluted to 60%.

The optimum acetate medium contained 0.1 *M* acetic acid, 1 x 10^{-5} *M* $Bi(NO_3)_3$ and 0.02% $NH_2OH \cdot H_2SO_4$, at pH 4.0. It was convenient to use a stock solution of 1 x 10^{-3} *M* $Bi(NO_3)_3$ in 9.5 *M* acetic acid plus 0.5 *M* sodium acetate. The 1:100 dilution of the stock solution in the sample gave the correct pH in unbuffered samples.

The polarography of Bi(III) has been studied extensively and was recently reviewed by Bond (32). His major conclusions were that the reversibility of the reduction of the chloride complexes correlated with the degree of complexation in the bulk solution. At sufficiently high chloride concentrations the reduction

was completely reversible. Other halide ions provided sufficient complexation in the double-layer for pseudo-reversible reduction but the aquo complex of bismuth was reduced irreversibly because of the slow removal of water from the ion.

In the chloride electrolyte used in the present work the reduction of the Bi-Cl complex cannot be observed because it overlaps the mercury oxidation process. NTA, of course, forms a stronger complex with bismuth, displacing chloride and giving a separate polarographic wave at a more cathodic potential.

No published data are available for the polarographic reduction of bismuth in an acetate medium, or for the formation of bismuth-acetate complexes. When we discovered empirically that an acetate electrolyte was advantageous for determining NTA, we undertook some studies to better understand the electrochemical process involved.

As a first step we attempted to define the presumed Bi-NTA complex in acetate electrolyte by the method of continuous variations. No stoichiometric relation could be determined. For all bismuth concentrations, including zero, a polarographic current proportional to the total NTA concentration was observed, but the proportionality constant increased with Bi concentration up to a slight excess of the 1:1 molar ratio of Bi:NTA. This may parallel the observation of Staroscik and Webs (28) that the polarographic current for In-NTA in an acetate medium decreased with increasing excess NTA, eventually yielding an adsorption wave.

We found, in the dc polarography of solutions containing no bismuth or less than 2:5 mole ratio of Bi:NTA, that $E_{1/2}$ = -0.21 to -0.24 V(SCE). The diffusion current "constant", I, was more nearly independent of mercury flow rate when calculated for the *total* NTA concentration than for bismuth or excess NTA concentrations. The wave shape corresponded to a pseudo-reversible process, with αn of 1.5 to 1.9. No ac polarographic wave could be observed in these solutions.

NTA appears to facilitate the reduction of bismuth by displacing water from the aquo complex and forming a 1:1 Bi-NTA complex in the double layer. However, the

mechanism of the diffusion-limited process in the absence of bismuth is unclear.

The effect of pH (between pH 1.5 and 4.5) was studied in solutions containing 1 x 10^{-5} *M* Bi and 5 x 10^{-6} NTA. The chloride medium contained 0.1 *M* total chloride and the acetate medium was made 0.02 *M* in acetic acid and 0.08 *M* in $NaClO_4$ for an equal ionic strength. The pH was adjusted with NaOH solution. In the chloride electrolyte, in contrast to the report of Afghan and Goulding (17), the peak current recorded in the PD mode increased sharply from pH 1.5 to pH 2.0 and changed little at further increases to pH 4.0, having a slight maximum at pH 2.5. In the acetate medium the peak current did not vary more than 10% over the pH range of 2.0 to 4.5, but showed a broad maximum at pH 3.0. In both systems the peak potential ($E_{1/2}$) shifted to more cathodic values with increasing pH. The shift over 2.5 pH units was about 50 mV in the acetate. Another study of four solutions at an ionic strength of 0.1 and pH 3.0 showed that increasing the total acetate concentration from 0.02 to 0.1 *M* had negligible effect on either the peak current or potential.

SECTION IV

RESULTS AND DISCUSSION

INSTRUMENT EVALUATION

The precisions attainable by the various instrumental techniques studied are best compared by reference to Table 7. In this table are presented the calibration results obtained with the optimum chemical and instrumental conditions.

The practical choice for an analytical application involves a balance between speed and convenience on one hand and precision on the other. Dual-cell PD has a distinct advantage in terms of precision and detection limits. However, it is slower than LS and there is relatively less to be gained from automation of the sample preparation. The P.A.R. instrumentation used in this project cost three times as much as the Chemtrix instrument; but the price differential might be substantially reduced by substitution of the P.A.R. Model 174 specialized analytical version for the Model 170. The Model 174 provides single- and dual-cell PD and LS capabilities at a price competitive with other LS instruments.

The Chemtrix Model SSP-5A is a compact, special-purpose instrument that provides as wide a range of programming variables as one is likely to need for the LS technique. The major problem in obtaining reproducible results appeared to be in setting the initial potential for the voltage scan. The small meter and manual potentiometer on the instrument made it difficult to set this value much closer than 0.1 V. The setting seemed to be reasonably stable when left untouched for repetitive measurements and it should be a simple matter to provide a fine-tuning adjustment to simplify arbitrary changes.

The Chemtrix drop timer and cell stand, in comparison with the P.A.R. model, was crude. The relay-actuated drop knocker was noisy and imparted considerably turbulence to the solution in the cell. Drop times were continuously adjustable by means of a potentiometer control and were not re-settable without a stop watch. The mercury stand did not provide for varying the height of the mercury column, except for a very

small differential adjustment between the cells.

Our Chemtrix instrument had a poor repair record. In the first twelve months transistors in the drop timer circuit were replaced three times. The plug-in amplifier module was replaced by the manufacturer four times and components of the amplifier were replaced in the field twice. Eventually, the entire instrument, including oscilloscope, was recalled by the factory for repair and calibration.

The great versatility of the Model 170 Electrochemistry System is provided at the cost of a rather bewildering set of controls. For routine measurements of the same type, however, only a few need to be adjusted individually. The effects of changing the available instrumental parameters were not investigated fully or systematically, although some such studies have been reported (33). Resolution can be improved at the cost of lengthening the analysis time by decreasing the potential scan rate. The analytical signal can be increased by increasing the pulse amplitude or the time of current sampling, both of which cause distortion and poorer resolution, and by increasing the drop time, which lengthens the analysis time.

The major operating problems involved sensitivity of detection. The nanoampere range of the Model 170 was nearly unusable because of a high noise level. In dual cell operation, there was an optimum pre-amplifier gain setting in the 174/51 module and an optimum current range setting on the Model 170. Also, the current offset and electrode balance controls, in dual-cell operation, required painstaking adjustment to avoid amplifier saturation.

The Model 170 was very reliable electronically, and no troubles developed in two years. After about three months of operation with the 174/51 dual-cell attachment, problems arose that seemed to involve both components. The routine trouble-shooting checks were inadequate to identify the source of malfunction and the entire instrument was returned to the manufacturer.

INDIUM

Calibrations

A number of calibration runs made under different conditions are summarized in Table 2. These include comparisons of seawater and sodium chloride as supporting electrolytes. Most were made by the PD technique, with a single cell. Each calibration run is internally consistent with respect to operating conditions but different runs are not necessarily comparable in sensitivity.

The parameters of mercury flow rate and potential scan rate, in particular, were not always the same. The effect of scan rate on the observed current (33) was not fully recognized at the time, but rates of 2 or 5 mV/sec were usually employed. The current is directly proportional to the area of the mercury drops, and a compromise can be made between sensitivity and analysis time most directly by varying the drop time. In these experiments the mercury flow rate was usually in the range 0.5 to 1.0 mg/sec and the drop time was one second.

Because of the above variations in experimental conditions the calibrations are best compared in terms of the linearity and scatter of the points. Table 2 gives the parameters for least-squares fits to the experimental points by the equation

$$Y(\text{nA}) = a + b\ X(\text{ppm NTA}) \qquad (1)$$

or, in the case of calibration by standard addition,

$$Y(\text{ppm found}) = a + b\ X(\text{ppm taken}) \qquad (2)$$

When the intercept a is enclosed in parentheses its value is smaller than its standard deviation. The table shows the effects of improved technique, since the relative standard deviations were about 10% for the first two runs and decreased to 1% in Run 9. Runs 3 and 4 were a direct comparison of sodium chloride and seawater electrolytes run at the same time; the slope of the calibration curve was anomalously low in sodium chloride.

Table 2

Calibration Runs for the Determination of NTA as the Indium Complex

Run	n, No. of Points	Concentration Range (ppm NTA)	a (nA)	b (nA/ppm	Std. Dev. of Fit (nA)	Remarks
1	14	0.2 - 2.0	(-5)	181	14	NaCl and seawater, combined, PD
2	9	0.2 - 2.0	-28	354	44	Seawater, PD
3	4	0.2 - 2.0	0.09	0.77	0.07	NaCl, std. addn., PD
4	4	0.2 - 2.0	0.07	0.98	0.08	Seawater, std. addn., PD
5	6	0.2 - 1.2	(7)	293	19	NaCl + 1.6×10^{-5} M $Na_5P_3O_{10}$, PD
6	6	0.2 - 1.2	(0.02)	0.99	0.05	NaCl, std. addn., PD
7	6	0.2 - 1.2	(0.03	1.00	0.05	NaCl, std. addn., PD
8	5	0.1 - 1.0	(0.4)	94	1.8	NaCl, LS
9	5	0.1 - 1.0	(-1.0)	272	2.8	NaCl, PD
10	7	0.1 - 3.2	(8)	152	21	60% Sewage effluent, LS
11	7	0.1 - 3.2	26	817	40	60% Sewage effluent, PD

The same solutions were used in Runs 5, 6, and 7. The method of standard additions was compared for two different operators in Runs 6 and 7, while a calibration curve was computed for the original solutions in Run 5. In this case, the relative standard deviation is lower for the addition technique (5%) than for the calibration curve (6.3%).

Runs 8 and 9 are a direct comparison of the single-cell PD (P.A.R.) and LS (Chemtrix), both in sodium chloride electrolyte. The relative standard deviation, at 1 mg NTA/ℓ, is 1% for the former and 2% for the latter. In 60% sewage effluent both techniques were much poorer (runs 10 and 11), with relative standard deviations of 5% for PD and 14% for LS. Two chart recordings from Run 11 are shown in Figure 2.

Interferences

The response to NTA in the range of 0.4 mg/ℓ was not significantly affected by EDTA, citric acid, or NaH_2PO_4 in varying proportions up to four times the concentration of NTA. The total indium concentration was 2×10^{-5} *M* in all cases. Table 3 shows recoveries (the fraction, in percent, of the concentration of the added species that was indicated by the analysis) of randomized concentrations of NTA from 0 to 2.0 mg/ℓ in the presence of 5×10^{-5} *M* Fe(III), Mn(II), Cu(II), or Bi(III). Under these conditions bismuth appeared to complex a significant portion of the NTA, leading to low results.

The effect of interferences might be mitigated by using the standard addition method of calibration. This approach assumes that a linear response to NTA would be observed, although the interferences might change the slope of the calibration curve. A test is summarized in Table 4, where 5 µg of NTA was added to 10 ml of the original solution. The initial concentrations of NTA were selected in a randomized order in the range 0.2 to 2.0 mg/ℓ. The trials of Fe(III) plus hydroxylamine were made at a constant level of NTA. A least-squares fit of the data gave the equation.

$$Y(\text{ppm NTA found}) = 0.11 + 0.95\ X(\text{ppm NTA taken}) \quad (3)$$

with a standard deviation of fit of 0.14 ppm.

Table 3

Recovery of NTA in the Presence of 5×10^{-5} *M* Fe, Mn, Cu, or Bi

NTA Taken	Fe(III) Found	Mn(II) Taken	Mn(II) Found	Cu(II) Taken	Cu(II) Found	Bi(III) Taken	Bi(III) Found
0.8 ppm	0.86	0.4	0.35	0.8	0.69	0.2	0.02
1.2	1.18	1.8	1.59	1.0	0.94	1.4	1.04
1.4	1.36	2.0	1.96	1.0	0.81	1.4	0.84
1.6	1.50			1.6	1.61	1.8	1.62

Table 4

Recovery of In-NTA in the Presence of Metals and Complexants

NTA Taken (mg/ℓ)	NTA Found (mg/ℓ)	Interference	Concentration x10^6, *M*
1.6	1.58	Cu	8
1.6	1.55	Cu	16
1.6	1.53	Zn	4
1.8	2.03	Zn	8
0.2	0.49	Mn(II)	4
1.8	1.98	Mn(II)	8
1.4	1.67	Bi	2
0.6	0.72	Fe(II)	8
1.2	1.16	Fe(II)	16
0.6	0.59	Fe(III)	8
1.2	.58	Fe(III)	16*
1.0	1.05	$N_2H_4 \cdot HCl$	40
1.0	0.81	N_2H_4+Fe(III)	12*
1.0	0.99	N_2H_4+Fe(III)	16
1.0	1.13	N_2H_4+Fe(III)	32
0.4	0.43	EDTA	8
1.0	1.61	EDTA	16*
0.8	0.88	$Na_5P_3O_{10}$	8
1.4	1.14	$Na_5P_3O_{10}$	16

* More than twice the standard deviation from the least-squares fit.

Three solutions, indicated in Table 4, deviated by more than twice the standard deviation and were not included in the calculation. The least-squares equation shows that the standard addition method tended to give high results, especially at lower concentrations, and that the precision was rather poor (14% relative standard deviation). Both results may be a consequence of a non-linear response to NTA in the presence of some or all of the additives.

Fe(III) interfered at 1.6×10^{-5} *M* but hydrazine effectively removed the interference. The high result for 1.6×10^{-5} *M* EDTA is a consequence of the standard-addition technique. After the addition of 0.5 ppm NTA the sum of NTA and EDTA concentrations was in molar excess of the total indium (2×10^{-5} *M*), causing a lower response for the standard addition.

Since Haberman (20) observed that a large excess of indium had to be added to some sewage samples to obtain a polarographic wave for free In, a few titrations were made. Indium solutions of 2 to 8×10^{-5} *M* concentration were prepared in three distilled water and three sewage effluent samples (15 ml of sewage effluent in a final volume of 25 ml) and the excess In was titrated with NTA by following the decrease in height of the In(III) wave in dual-cell LS. Although two of the effluent samples had very little excess In (2×10^{-5} *M* total concentration) the results indicated 1.7 to 1.9×10^{-5} *M complexed* indium, corresponding to an indium-complexing power of the original effluent of 3×10^{-5} *M*.

As noted by Haberman (20) NTA did not release In from this complex in a polarographically determinable form. The mean slopes of the three titrations in distilled water corresponded to 1.7 moles of In removed per mole of NTA. The corresponding value in the effluent samples was 1.4 moles of In per mole of NTA. These numbers probably do not represent a stoichiometric complex, but reflect an accumulation of NTA in the double layer surrounding the mercury drop. Staroscik and Webs (28) observed that, for an increasing excess of NTA, the In-NTA wave decreased in height and eventually was transformed to an ill-defined adsorption wave.

BISMUTH, CHLORIDE MEDIUM

Calibrations

Since an analytical procedure had already been developed (17) and applied to seawater samples (31), relatively little was done in the way of evaluating specific interferences or in modifying the procedure. Calibration runs were made primarily to evaluate the instrumentation, particularly for PD. Five such calibrations, made early in the project, are summarized in Table 5, in which the parameters for least-squares fits of equation 1 are shown in the same format as in Table 4. The most noteworthy point is the great variation in precision. The relative standard deviations range from about 1% (Run 1) to 13% (Run 4). The poor precision is believed to result more from unfamiliarity with the instrument than from the chemical procedure. Typical chart recordings, taken from Run 3, are shown in Figure 3.

Interferences

Although Afghan *et al.* (17) found that copper did not interfere in the determination of the Bi-NTA complex and that Bi quantitatively displaced Cu from its NTA complex at 2×10^{-5} *M* concentration, other workers have not confirmed these results. Gahler (31) found that in the presence of 2 mg Cu/ℓ, the concentration of NTA indicated by a dc polarographic measurement was high, and Taylor *et al.* (6), using the same type of instrumentation and procedure as Afghan (17) observed an interference in tap water that they believed to result from copper. Figure 4 shows traces obtained by LS of solutions containing NTA and Cu. Curves 1, 2, and 3 correspond to solutions of 2 mg NTA/ℓ and curve 4 to a 1 mg NTA/ℓ solution, Curves 3 and 4 were obtained with 1×10^{-5} *M* Cu, Curve 2, with 0.5×10^{-5} *M* Cu, and Curve 1, with no copper. The test and reference solutions all were 0.1 *M* in NaCl, and 1×10^{-5} *M* in Bi at pH 2.0.

A better test of the analytical procedure would have been obtained with NTA and Cu, but no Bi, in the appropriate reference solutions. These results, however, show that the copper peak precedes and interferes with the Bi-NTA wave. There is no indication that copper

Table 5

Calibration Runs for the Determination of NTA as the Bismuth Complex in Chloride Electrolyte

Run	n, No. of Points	Concentration Range (ppm NTA)	a (nA)	b (nA/ppm)	Std. Dev. of Fit (nA)	Remarks
1	5	0.2 - 1.6	-68	648	8	NaCl (PD)
2	9	0.2 - 1.8	(-18)	375	24	NaCl (PD)
3	8	0.2 - 2.0	(-6)	374	17	Seawater (PD)
4	9	0.2 - 2.0	(-1)	395	52	NaCl
5	9	0.2 - 1.0	(9)	209	7	Seawater (LS)

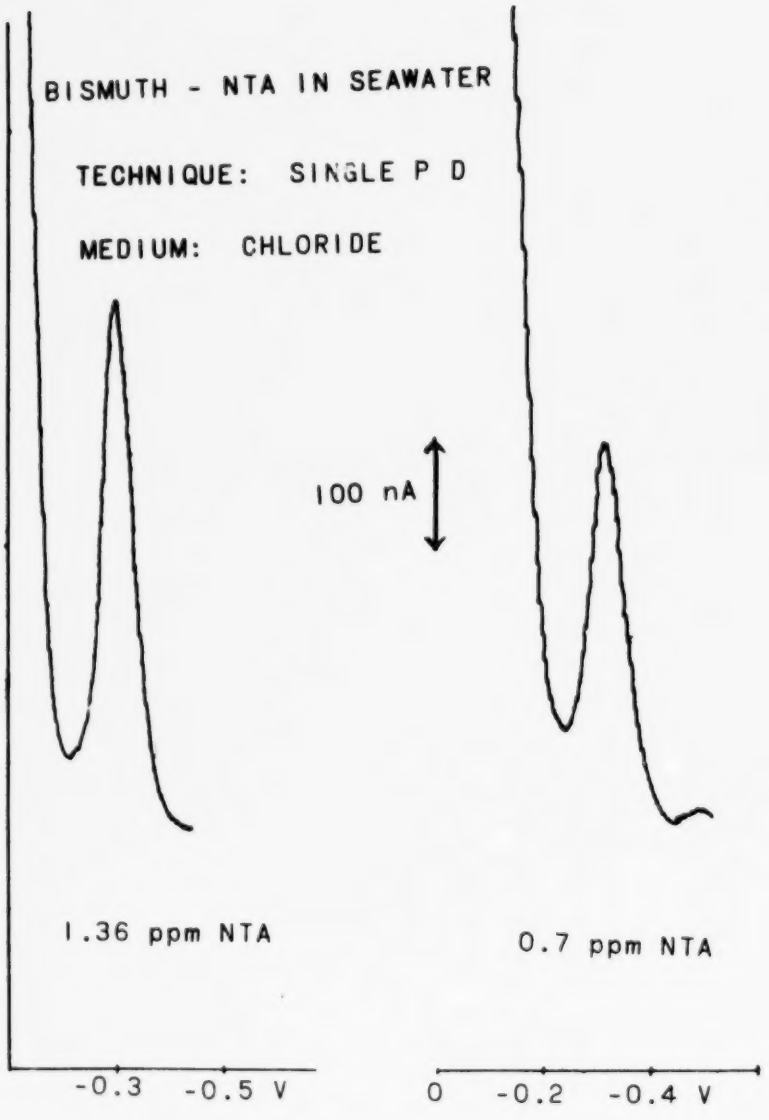

Figure 3. Determination of the bismuth-NTA complex in seawater by pulse differential polarography

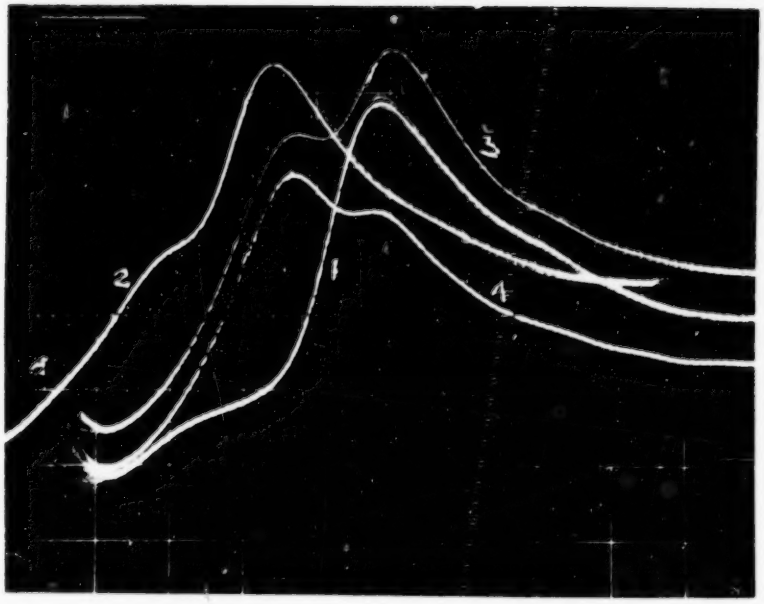

Figure 4. Copper and bismuth-NTA waves by linear sweep voltammetry

complexes any NTA at pH 2.0.

When the method was tried in waste waters difficulties appeared, particularly in trying to match the sample and reference scans in the LS technique. Figure 5 shows some typical results obtained with the Afghan (17) procedure in an effluent from a small activated-sludge plant serving a residential development in Clarke County, Georgia. The fresh sample was filtered through 0.45 μ Millipore but no preservative was added. Figure 5(a) shows the sample (A) and reference (B) scans, as well as the difference, for no added NTA; thus, the only difference between the cells is 1×10^{-5} *M* Bi added to cell A. Figures 5(b) and 5(c) were taken at a later time but for the same effluent and procedure. Curves 4, 1, and 2, respectively, of Figure 5(b) are the difference traces for 0.5, 1.0, and 2.0 mg NTA/ℓ. In Figure 5(c), curves A and B are for sample and reference, respectively, and 1 is the difference, for 0.2 mg NTA/ℓ in A, while Curve 2 is the difference trace for 1.0 mg NTA/ℓ. For more than about one ppm of NTA fairly satisfactory traces and calibration curves were obtained, but at lower concentrations of NTA the problem of matching the cells was more severe.

This difficulty in determining low levels of NTA in natural or waste waters is further illustrated in Figure 6, which shows calibration curves obtained in the above sewage effluent and in Oconee River water, by both LS and PD techniques. The slopes of the curves are strikingly different for the two sources, showing that a calibration based on distilled water standards would be highly inaccurate for at least one of the samples. Because of the non-zero intercepts of the curves in Figure 6, the method of standard additions would not be a great improvement and could not be used for low levels of NTA. The parameters of the least-squares equations for these calibrations are given in Table 6.

Interference from sulfur compounds in some sewage samples has been reported (17), and treatment with hydrogen peroxide was recommended. We were not able to achieve any improvement through hydrogen peroxide treatment and found it difficult to remove the excess

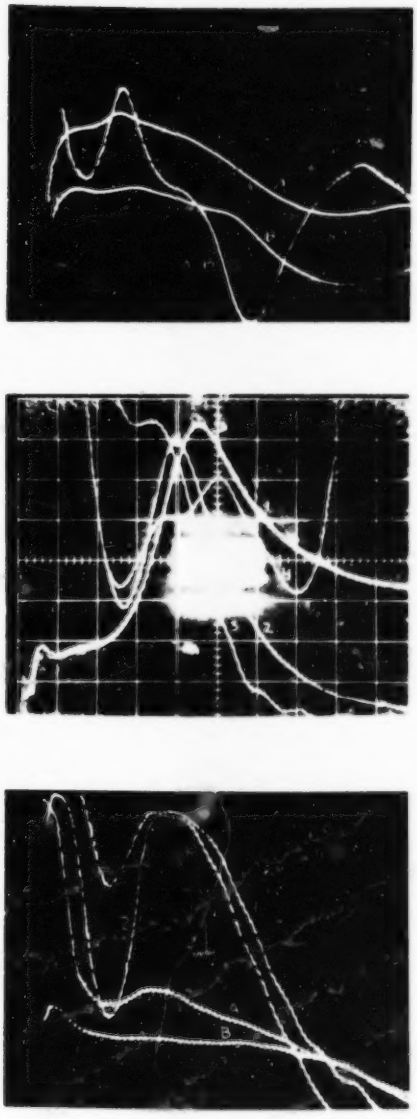

Figure 5. Effect of sewage effluent on the bismuth-NTA polarographic wave in chloride electrolyte

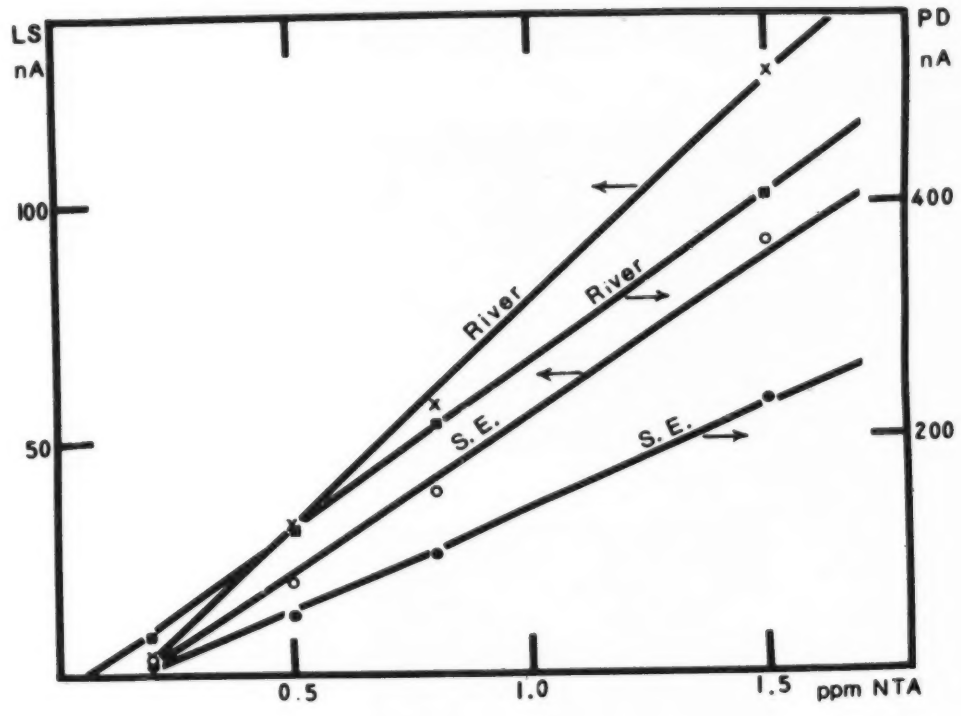

Figure 6. Calibration curves for the determination of the bismuth-NTA complex -- chloride electrolyte

Table 6

Calibration Runs for Bi-NTA in Chloride Electrolyte--
Sewage Effluent and River Water

	rel. std. dev. at 1 ppm NTA
Occnee River, PD Technique Y(nA) = (-18±4) + (286±5) X (mg NTA/ℓ),	1.7%
Oconee River, LS Technique Y(nA) = (-16±2) + (95±2) X (mg NTA/ℓ),	2.4%
Sewage Effluent, PD Y(nA) = (-32±7) + (175±8) X (mg NTA/ℓ),	5.3%
Sewage Effluent, LS Y(nA) = (-13±3) + (69.0±3.6) X (mg NTA/ℓ),	6.1%

peroxide sufficiently. About this time we discovered that an acetate electrolyte gave greatly superior results in waste waters and we discontinued investigation of the chloride medium.

BISMUTH, ACETATE MEDIUM

Calibrations

Calibrations in the acetate medium are summarized in Table 7. The experiment of Run 1 was a balanced, incomplete block design for testing four levels of NTA in four sources of water, in duplicate. The standard deviation of the duplicates was 13 nA, including one pair that differed by 43 nA (the outlier was *not* discarded). No significant effects were found for the water sources, which included distilled, tap, river water and sewage effluent. Accordingly, the results were pooled for the calibration shown in Run 1.

Another similar balanced, complete block design was used to compare the LS and PD techniques using six sources of water: distilled, tap, woodland stream, Oconee River, and effluent from a small activated sludge treatment facility and from a municipal sewage treatment plant. No significant differences due to source were observed in the LS mode, and the pooled results are summarized in Run 2. For the PD results source effects were significant at the 95% level of significance and the data have been subdivided. The potable and natural waters are combined in Run 3 and results for the two effluents are summarized in Run 4. The effluents gave a somewhat lower response to NTA than the "clean" waters but gave somewhat better precision.

A direct comparison of calibration in distilled water and in sewage effluent, both by PD, is shown in Runs 7 and 8. These were made at higher concentrations of NTA and the bismuth concentration was increased to 5×10^{-5} *M*. Both lines show negative intercepts (a) greater than their standard deviations, corresponding to about 0.2 mg NTA/ℓ, but the slopes of the calibration curves are essentially identical and the precision is somewhat better in the effluent. The much lower response factor (b) in comparison with Runs 1, 3, or 4 results from a change of capillaries, differing by a factor of nearly three in mercury flow rate.

Table 7

Calibration Runs for the Determination of NTA as the Bismuth Complex in Acetate Electrolyte

Run	n, No. of Points	Concentration Range (ppm NTA)	a (nA)	b (nA/ppm)	Std. Dev. of Fit (nA)	Remarks
1	24	0.05 - 0.50	(1.5)	313	11	PD; four types of water source
2	24	0.2 - 1.5	(0.1)	77.8	4.5	LS (Chemtrix); six types of water source
3	16	0.2 - 1.5	(3)	339	20	PD; four types of "clean" water
4	8	0.2 - 1.5	(3)	308	7	PD; two sewage effluents
5	8	0.05 - 0.2	2.9	40.6	0.9	LS (Chemtrix); distilled water
6	5	0.2 - 0.8	-22	347	3	PD; distilled water plus $NaClO_4$
7	4	1 - 4	-35	164	19	PD; distilled water
8	4	1 - 4	-30	162	4	PD; sewage effluent

Table 7 (cont'd)

Calibration Runs for the Determination of NTA as the Bismuth Complex in Acetate Electrolyte

Run	n, No. of Points	Concentration Range (ppm NTA)	a (nA)	b (nA/ppm)	Std. Dev. of Fit (nA)	Remarks
9	5	0.01 - 0.12	(-.1)	354	0.6	Dual PD; distilled water
10	7	0.01 - 0.1	-1.0	99.0	0.5	LS(PAR); distilled water
11	10	0.01 - 0.1	0.6	242.4	0.8	Dual PD; stream water
12	9	0.02 - 2.0	-26	669	39	PD; sewage effluent
13	12	0.02 - 2.0	(5)	857	23	Dual PD; sewage effluent

When the dual-cell modification of the P.A. R. Model 170 was obtained a comparison of LS and PD modes on the same instrument was made in Runs 10 and 11. Single-cell and dual-cell PD operation were compared in Runs 12 and 13. The high precision attainable with dual-cell PD is indicated in Runs 9, 11, and 13. Chart records for the complete calibration Run 9 are shown in Figure 7, and for the two lowest concentrations of Run 11 in Figure 8.

A demonstration of the presence of NTA in raw and treated municipal sewage is shown in Figure 9. Samples from the Athens Oconee treatment plant were preserved with 1% formaldehyde and filtered through 0.45 μ Millipore. The samples were analyzed by the dual-cell PD technique in acetate electrolyte. The raw sewage gave a peak of about 3.0 nA, which increased to 21.5 nA when the cell was spiked with 0.1 mg NTA/ℓ. The effluent sample gave a peak of 2.0 nA, increasing to 19.5 nA when spiked with 0.1 mg NTA/ℓ. These results indicate 16 and 11 μg/ℓ, respectively, in the cells, or about 30 and 20 μg NTA/ℓ in the original raw and treated samples. Since the standard deviation of the corresponding calibration was equivalent to 4 μg NTA/ℓ, the difference between the samples may not be real, although some degradation of the NTA in the treatment process would be expected. Instrumental problems prevented confirmation or further study of NTA in natural samples.

Interferences

In preliminary studies of the effects of metal ions on the determination of NTA, Fe(III) and Cu(II) seemed to interfere most significantly. Heating the sample with at least 0.02% of either hydrazine sulfate or hydroxylamine hydrochloride, as in the chloride procedure (17), effectively removed all interference from iron at concentrations up to 1×10^{-5} *M* (0.5 ppm).

In the presence of 1×10^{-5} *M* Cu, NTA recoveries were about 80-90% and were quite variable. Although the problem seemed to be associated with low concentrations of chloride ion, it was not completely explained or solved. In the acetate medium, free of chloride, separate waves were observed for Cu(II), Bi(III), and Bi-NTA at half-wave potentials of +0.07, -0.005, and -0.16V (*vs.* SCE), respectively. In the presence of

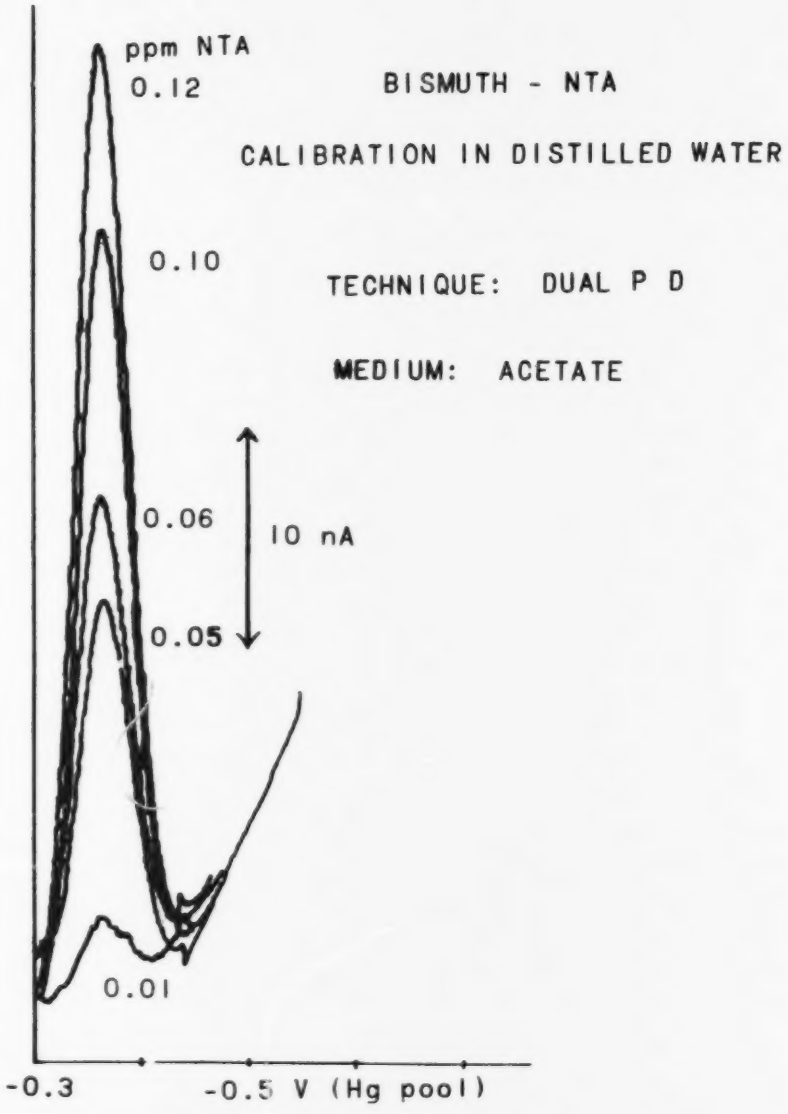

Figure 7. Determination of the bismuth-NTA complex in distilled water by dual cell pulse differential polarography

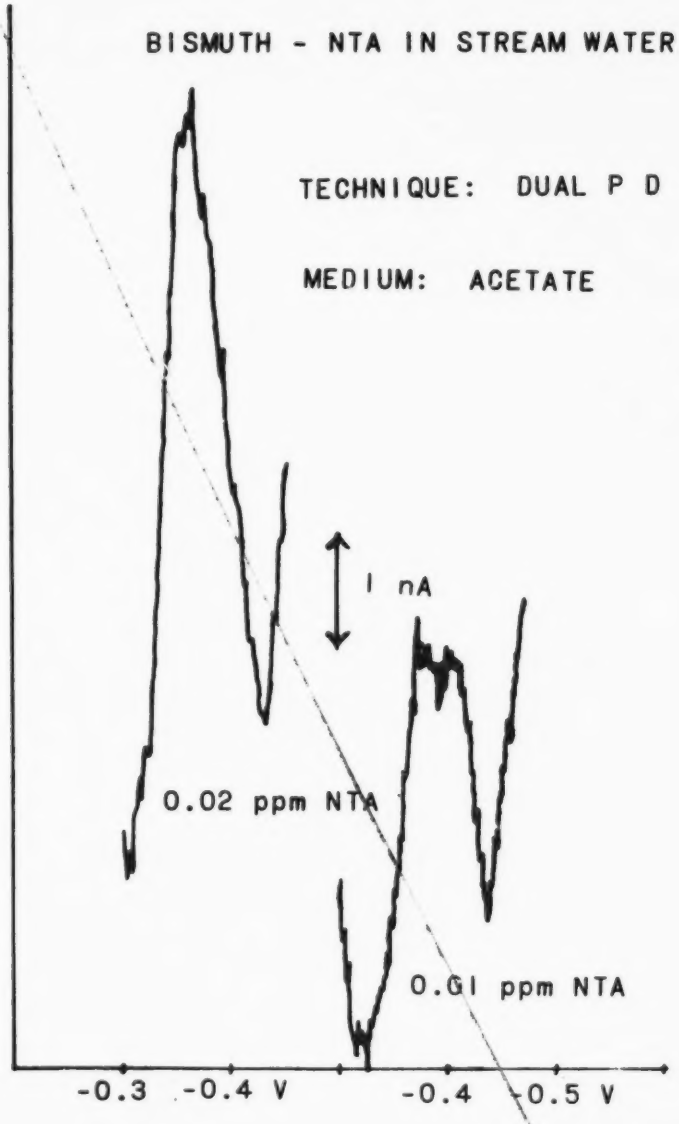

Figure 8. Determination of the bismuth-NTA complex in distilled water by dual cell pulse differential polarography

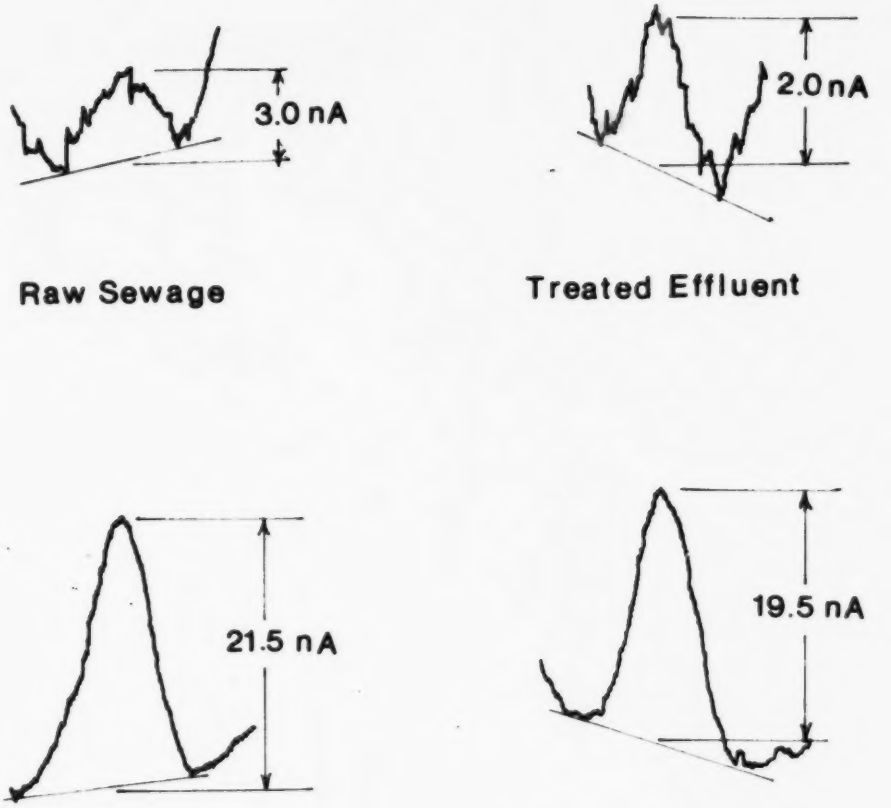

Figure 9. Differential pulse polarographic estimation of NTA in raw and treated municipal sewage

0.02% hydroxylamine hydrochloride (3×10^{-3} *M*) or 0.1 *M* sodium chloride, the Cu(II) wave at +0.07V disappeared and was replaced by a very large wave at +0.21V, which may be due to mercury oxidation. These potentials were measured with a mercury-mercurous sulfate reference electrode having a potential of +0.360V *vs.* SCE. EDTA was tried as a masking agent for copper but had no effect, probably because bismuth was able to displace copper from the EDTA complex.

Both copper and chloride might be expected in natural and waste waters at the concentrations used in these studies and the analyst should be aware of the possibility of low results for NTA due to copper. The calibration results reported in the preceding section, however, did not reveal any problems in applying the method to a variety of water sources.

A number of possible interferences were investigated by single-cell PD at NTA concentrations of 0.2, 0.5, and 1.0 mg/ℓ. The average recovery was calculated from the slope of the best calibration curve through the origin for each set of NTA concentrations, relative to standards prepared in the same Occnee River water but without added metals or complexants. The results are summarized in Table 8. Lead, at 1×10^{-4} *M* concentration, caused a low recovery of NTA but did not interfere significantly at 1×10^{-5} *M*. High concentrations of calcium and magnesium (400 mg/ℓ) also led to low recoveries of NTA but no other interferences were found. Citric acid, at 1×10^{-5} *M* concentration, was included in several of the preliminary tests with no perceptible effect on the response to NTA.

Table 8

Recovery of Bi-NTA in the Presence
of Metals and Complexants in Acetate Electrolyte

Interference	Average Recovery, Percent
Fe(III), $1x10^{-5}$ *M*	101
Fe(III) + Mn(II), each $1x10^{-5}$ *M*	100
Fe(III) + $Na_5P_3O_{10}$, each $1x10^{-5}$ *M*	97
Mn(II), $1x10^{-4}$ *M*	103
Pb(II), $1x10^{-4}$ *M*	78
Pb(II), $1x10^{-5}$ *M*	96
Cd(II), $1x10^{-4}$ *M*	98
Zn(II), $1x10^{-4}$ *M*	99
Ca(II), 400 mg/l ($1.0x10^{-2}$ *M*)	49
Mg(II), 400 mg/l ($1.7x10^{-2}$ *M*)	72
PO_4^{3-}, $1x10^{-5}$ *M*	103
$Na_5P_3O_{10}$, $1x10^{-4}$ *M*	97

SECTION V

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SECTION VI

APPENDIX

RECOMMENDED NTA ANALYSIS PROCEDURES

SALINE WATERS - MORE THAN 0.1% CHLORIDE

Reagents

1 *N* Hydrochloric Acid

1 *M* Sodium or Potassium Chloride

1 x 10^{-3} *M* Bi: Dissolve 50 ± 2 mg

$Bi(NO_3)_3 \cdot 5H_2O$ in 100 ml 1 *N* HCl.

1% Hydroxylamine Hydrochloride

NTA stock solution, 2 g/l. Dissolve 1.434 g $C_6H_6O_6NNa_3 \cdot H_2O$ in 500 ml distilled water.

Procedure

Place 5.0 ml of sample in each of two 10-ml volumetric flasks and add 0.2 ml of 1% hydroxylamine hydrochloride to each. Add 0.1 ml of 1 *N* HCl to the reference and 0.1 ml of 1 x 10^{-3} *M* Bi to the sample flask. If the original sample contained less than about 0.5% chloride, add 1.0 ml of 1 *M* chloride solution to each flask and dilute to the mark with distilled water. If the original water sample contained more than about 0.5% chloride do not add additional salt solution, but dilute to the mark with distilled water. Place 3.0 ml of sample and reference solutions in the respective cells, de-aerate for 10 minutes, and run a polarographic scan from about -0.2 to -0.4 V *vs.* the mercury pool anode. Compare the peak currents with those for standard solutions similarly prepared with freshly diluted NTA stock solution. The procedure is applicable to NTA concentrations from 0.05 to 5.0 mg/l.

NATURAL AND WASTEWATERS - LESS THAN 0.1% CHLORIDE

Reagents

Acetate electrolyte, 9.5 *M* in acetic acid plus 0.5 *M* in sodium acetate.

1×10^{-3} *M* Bi: Dissolve 50 + 2 mg $Bi(NO_3)_3 \cdot H_2O$ in 100 ml of the acetate electrolyte.

1% Hydroxylamine sulfate solution

NTA stock solution, same as above.

Procedure

Place 5.0 ml of sample in each of two 10-ml volumetric flasks, add 0.2 ml of 1% hydroxylamine sulfate solution to each and heat nearly to boiling. Cool to room temperature and add 0.1 ml of acetate electrolyte to the reference and 0.1 ml of 1×10^{-3} *M* bismuth solution to the sample. Dilute each to the mark with distilled water, mix, and place 3.0 ml in the respective cells. De-aerate for 10 minutes and run a polarographic scan from -0.1 to -0.3 V (*vs.* SCE). The mercury pool anode can be used as a reference but its potential is apt to vary with different sample sources. It is preferable to use an external reference electrode with a sodium perchlorate salt bridge to both cells. Compare the peak currents with those for standard solutions similarly prepared from freshly diluted NTA stock solution. The procedure is applicable to NTA concentrations from 0.01 to 5.0 mg/l.

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